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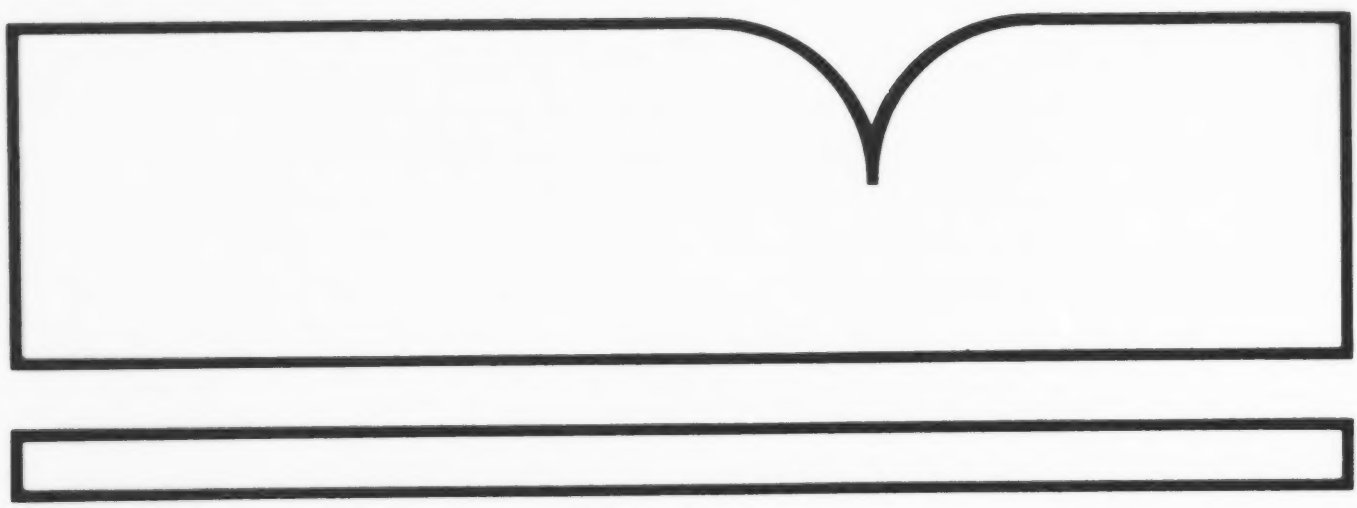

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PILOT SCALE TREATMENT OF AQUEOUS METAL AND CYANIDE BEARING HAZARDOUS WASTES

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PILOT SCALE TREATMENT OF AQUEOUS METAL AND CYANIDE BEARING HAZARDOUS WASTES

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ABSTRACT

The US Environmental Protection Agency (EPA) has been directed to evaluate the performance of various technologies for the treatment and/or destruction of certain wastes that are presently undergoing land disposal. As a part of the US EPA alternative technologies research program, the University of Cincinnati is testing existing treatment technologies that are applicable to metal and cyanide bearing hazardous wastes at the US EPA Test & Evaluation Facility in Cincinnati, Ohio. The units which have been designed and fabricated for testing are: lime precipitation, sulfide precipitation, mixed-media filtration, ion exchange and alkaline chlorination of cyanide.

INTRODUCTION

Under the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments (HSWA), EPA will be promulgating new regulations involving the treatment and land disposal of hazardous wastes. An estimated 7.9 billion gallons of toxic metal-bearing wastes and 4.7 billion gallons of cyanide wastes were generated in the U.S.A in 1983 (Grosse).

The U.S. EPA is interested in defining treatment technologies for these wastes and evaluating the performance of each technology/waste combination.

In the absence of preferred technology/waste field demonstration data and for the purpose of confirming field test results, the EPA has been directed to perform in house bench-scale and pilot-scale testing. EPA's Test and Evaluation (T&E) Facility in Cincinnati, Ohio, has been selected as a suitable location to carry out these pilot-scale studies. The T&E Facility is serviced by 24,000 sq. ft. of high bay area, 2 overhead cranes, 2 high gates for truck/tanker entrance, 2 process control laboratories, a machine shop, green house and office spaces. At present, approximately 16 pilot-scale and 4 bench-scale projects are being operated at the T&E Facility. The College of Engineering of the University of Cincinnati (UC), is operating the facility and providing the technical support for various test projects including the "Hazardous Waste Treatment Technology Assessment" program.

One objective of this research program is to fabricate and install pilot-scale units for different technologies on the basis of established industry process parameters. Once a potential waste has been identified, a complete analysis of the waste is performed using EPA-approved methods. Then, bench-scale process optimization studies are conducted to optimize pilot-scale process parameters. Finally, performance evaluation tests are conducted on the pilot-scale unit(s) of interest. In the event that a real waste can not be obtained due to permitting limitations or source

location, a surrogate waste is prepared on the basis of available information. Bench-scale optimization is performed using the surrogate waste followed by preliminary testing of the selected unit processes.

The source of the wastewater for the experiments described in this paper was a local Cincinnati metal finisher who has been involved in joint EPA-industry demonstration projects in the past. The metal finishing plant is a multi-process facility which incorporates both automatic and mechanical barrel, rack and hoist operations for zinc, brass, chromium, tin, bright nickel and cadmium plating. This plant operates a waste treatment system that segregates the waste into three different streams:

1) Mixed acid/alkali metal rinse baths devoid of Cr^{+6} and CN (EPA RCRA codes D006/D008)
2) CN process streams and rinses (EPA RCRA codes F007 and F009)
3) Cr^{+6} process streams from chrome plating baths (EPA RCRA codes D007)

Additional spent bath solutions were used to increase the metal concentrations in the wastewater. The wastes supplied for each run are discussed in detail in the results section below.

Safe handling of these wastes was a matter of serious concern during the early planning of this project. Every effort was made to comply with the regulations and guidelines which govern the handling of these types of hazardous wastes. The work reported in this paper is divided into two phases: Phase I - the preliminary testing of the installed metal-removal process units using a typical waste stream from a local metal finishing

company and Phase II - the treatment of a selected cyanide waste (F007) which is currently being investigated.

PHASE I

DESIGN AND PRELIMINARY TESTING OF THE PILOT-SCALE UNITS

During the first phase of this project, the main objective was to fabricate, install and test a pilot-scale demonstration treatment train consisting of conventional technologies which are currently being used in the electroplating and metal finishing industries for metals removal from wastewater. They are: neutralization/precipitation, flocculation/clarification and mixed-media filtration. In addition, several advanced technologies were selected for testing, including: sulfide precipitation and ion exchange polishing. Following a comprehensive literature review, field trips were made to the local metal finishing company to view the actual process operations and to collect samples for preliminary waste characterization.

Initial design of the process units was based upon common practices observed by the metal finishing industry, as reported by Durney (1984), Peters (1985), Patterson (1985) and Sanks (1978). The initial design flow rate was 2.5 gallons per minute. Two precipitation systems were tested: lime precipitation with unaided flocculation and enhanced lime/sulfide precipitation with polyelectrolyte-aided flocculation. In each case, polishing techniques such as mixed-media filtration and ion exchange adsorption were used. A schematic including these two precipitation options of the treatment train are shown in Figure 1. A brief description

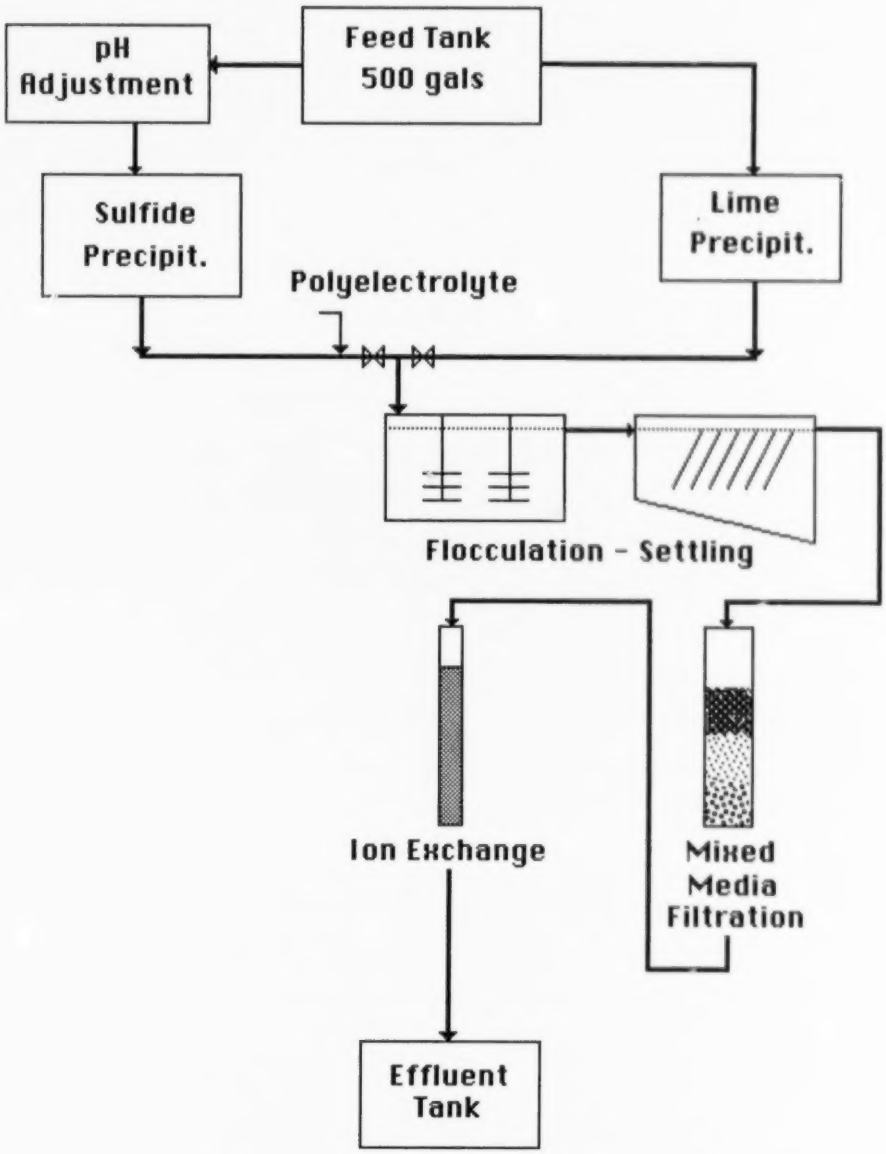

Figure 1. Schematic of the phase I treatment trains

for each of the unit processes is given below.

1) Lime precipitation: The residence time in the neutralization/ precipitation tank was 30 minutes. A proportional pH controller was used to control the pH within ± 0.2 units of the desired value. A 10% lime slurry was used as the reagent and the dose of the lime slurry was controlled by the pH controller.

2) Flocculation: A two chambered flocculation unit provided a total residence time of 60 minutes. Each compartment contained a slow speed agitator to aid the coagulation process. During the enhanced lime/sulfide precipitation a general purpose anionic polyelectrolyte was used to accelerate the process of coagulation. Jar tests provided an optimum dose of 54 mg/L.

3) Clarification: A plate settler was designed for the clarification step utilizing sixteen 2 ft. by 2 ft. inclined plates. The resultant loading rate was 56.25 gpd/ft^2. The plates were installed with an adjustable inclination to the horizontal. All sixteen plates were connected to form a single unit module which could easily be removed for cleaning. Although a 75° inclination was set for general operation, it could be increased up to 90° to avoid sludge accumulation on the plates. The bottom of the settling tank was inclined with a grading of 13:48 along its length to concentrate all the sludges towards the drain. After each run, the sludges were drained into drums and the settling tank was flushed. The retention time for the settling tank was 48 minutes.

4) Mixed-media filtration: Mixed-media filters were used to remove fine suspended particles not settled during the clarification step. A 12 inch plexiglass column was used for the mixed-media filtration system with a second column serving as a backup. The media were stratified into three layers where an 18 inch anthracite layer on top was followed by a 15 inch sand layer with an 8 inch support layer of gravel at the bottom. The effective sizes of anthracite and sand particles were 1.05 mm and 0.45 mm, respectively. These sizes were selected to ensure that the media could be backwashed without intermixing the anthracite and the sand layers. The surface loading rate was 3.79 gpm/ft^2 and the calculated pressure drop across the bed for such loading rate is 1 ft. of clear water.

5) Sulfide Precipitation: Insoluble sulfide precipitation (ISP) was tested for this study using a 10% FeS slurry as the reagent. The dosage selected on the basis of available literature information was 380 mg/L. FeS slurry was added into a reactor preceding the flocculation tank. A 10 minute residence time was used in the sulfide reactor. The pH of the feed coming out of the preceeding neutralization tank was adjusted to 10.5.

6) Ion Exchange: Ion exchange was used as a polishing technique following conventional treatment. The resin, selected for this research project, was a crosslinked macroreticular cation exchange resin with unique chelating functionality highly suitable for heavy metal removal. The cation exchange capacity of the resin was

1.0 meq/ml of wet resin. A six inch column was loaded with 0.5 ft^3 of resin. The resulting loading rate was 5 gpm/ft^3, which is the upper limit of the range recommended by the manufacturer. Regeneration of the cation exchange resin was accomplished by passing a 5% hydrochloric acid solution through the bed followed by the addition of a 4% sodium hydroxide solution which completes the conversion of the resin to the sodium form. Finally, the resins were rinsed with water to free them of excess sodium hydroxide. Usually, 10 gallons of acid solution was required per cubic feet of resin for regeneration followed by 20 gallons of sodium hydroxide solution for neutralization. Approximately, 75 gallons of water was used per cubic foot of resin for the rinse wash.

RESULTS

During the first phase, a total of four runs were conducted on the wastes provided by the metal finishing plant. Two shakedown runs were performed to evaluate the treatment system's performance. The other two runs were actual test runs where two different treatment trains were tested for mixed acid/alkali metal rinse wastewater. Results of these two test runs are described below.

Treatment Train # 1

The unit processes used for this treatment train were: lime precipitation (pH of 9.5), unaided flocculation, clarification, mixed-media filtration and ion exchange. The mixed acid/alkali metal waste contained cadmium, trivalent chromium, copper, iron, nickel, lead

and zinc. In addition to the high metal concentrations (total of 685 mg/L), this waste contained degreasers and chelating agents. Ammonia was evident by the smell and suspended solids were visible in the feed. Concentrations of various metals in the feed and in the effluents from different unit processes are presented in Table 1 and cumulative percentage removal data are shown in Table 2.

TABLE 1. Process Unit Effluent Quality
Treatment Train # 1

	Concentrations (mg/L)						
	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Feed	176.5	52.2	26.5	19.8	128.7	2.7	278.8
Effluents from:							
Clarifier	48.5	6.1	22.9	1.7	113.7	<0.5	45.8
Mixed-media	38.7	3.1	22.1	0.4	113.2	<0.5	23.0
Ion Exchange	0.24	2.45	3.56	<0.3	22.5	<0.5	23.1

TABLE 2. Cumulative Removal Efficiencies
Treatment Train # 1

	Cumulative Removal %						
	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Clarifier	72.5	88.3	13.6	91.4	11.7	>81.5	83.6
Mixed-media	78.1	94.1	16.6	98.0	12.0	>81.5	91.8
Ion Exchange	99.8	95.3	86.6	98.5	82.5	>81.5	91.7

The basic lime precipitation system removed >80% of Cr, Fe, Pb, and Zn. Although 73% of Cd was removed, Ni and Cu exhibited poor (<15%) removal

efficiency. It is assumed that these elements were complexed with either ammonia or with some other component of the waste, hence, impeding precipitation. The mixed-media filters provided little additional treatment. On the other hand, the ion exchange units, showed marked improvement in effluent quality except for zinc and trivalent chromium.

Treatment Train # 2

The second treatment train consisted of enhanced lime/sulfide precipitation (pH of 10.5), polymer aided flocculation, clarification, mixed-media filtration and ion exchange. A second ion exchange column with 0.5 ft^3 of resin was used to increase the polishing capacity. The main objective was to determine how removal efficiency can be improved with an enhanced precipitation system. Although the second batch of waste was similar to the first it was not identical. The composition of the second batch of waste, as shown in Table 3, indicates that it contained greater amounts of Pb and Zn and slightly lower concentrations of Cd and Ni than the first batch.

Metal concentrations for the various unit process effluents are shown in Table 3 with the cumulative percentage removals given in Table 4. The enhanced lime/sulfide precipitation system resulted in better clarifier effluents and a higher percentage of removal for all the metals analyzed. This is shown by the bar graphs in Figure 2 below. Removal of Cr, Fe, Pb and Zn by the enhanced precipitation system exceeded 90%. However, the enhanced precipitation system did not solve the problems related to the treatment of Cu and Ni, by yielding only 31% and 14% removal efficiencies,

TABLE 3. Process Unit Effluent Quality
Treatment Train # 2

	Concentrations (mg/L)						
	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Feed	194.6	60.1	29.0	17.4	98.6	22.2	415
Effluents from:							
Clarifier	26.4	3.2	20.0	0.6	85.3	<0.5	31.1
Mixed-media	24.3	2.1	22.7	<0.3	85.3	<0.5	30.9
Ion Exchange	0.4	1.4	2.3	<0.3	13.4	<0.5	0.4

TABLE 4. Cumulative Removal Efficiencies
Treatment Train # 2

	Cumulative Removal %						
	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Clarifier	86.4	94.7	31.0	96.6	13.5	>97.7	92.5
Mixed-media	87.5	96.5	21.7	>98.2	13.5	>97.7	92.6
Ion Exchange	99.8	97.7	92.1	>98.2	86.5	>97.7	99.9

respectively. Performance of the mixed-media filtration and ion exchange units were similar to results obtained from the preceding test run (treatment train #1), with one exception; the fresh ion exchange resin, added to the second column in series, was able to lower the concentration of Zn from 30.9 mg/L to 0.4 mg/L.

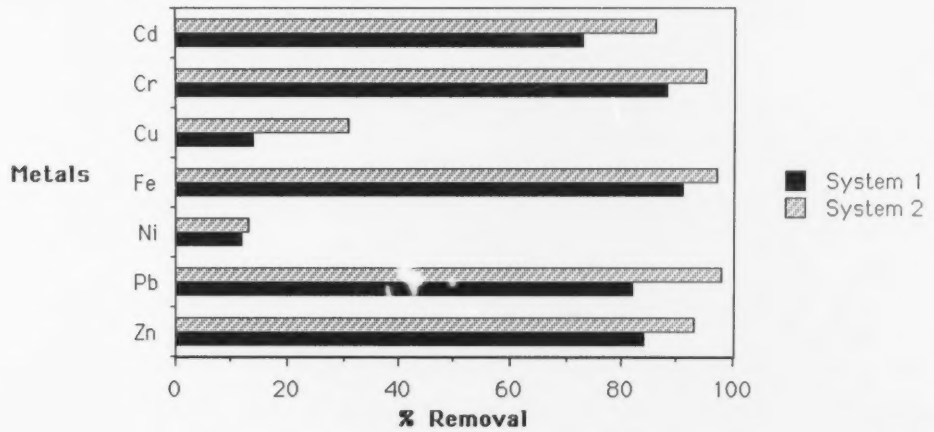

Figure 2. Removal efficiencies of the two precipitation systems

All the metal concentrations were measured by atomic absorption spectrophotometer. Standard EPA methods, as listed in Table 5, were utilized. Calibration and check standards were run at the beginning of each set of analyses for the specific metals to be measured. Check standards, as well as, a duplicate and spike were run per set of ten samples. A 10% maximum deviation for precision and a 70-130% spike recovery were tolerated.

TABLE 5. Analytical Methods for Metals

Metals	Methods*	Metals	Methods*
Cadmium	213.1, 213.2	Chromium	218.1, 218.2
Copper	220.1, 220.2	Iron	236.1
Nickel	249.1	Lead	239.1, 239.2
Zinc	289.1, 289.2		

* Ref: Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Rev. March 1983.

PHASE II

ALKALINE CHLORINATION FOR CYANIDE DESTRUCTION

The second phase of research will focus on a comprehensive waste characterization, process optimization for each waste and continuous monitoring of all significant parameters during pilot-scale operation. A complete study of two cyanide waste streams (F007) are being planned for the rest of the calendar year 1987. Two different concentration levels have been selected for testing: 400 ppm cyanide and 1000 ppm cyanide.

After preliminary testing of the first two treatment trains was completed, it became evident that the process flow and sizing of the treatment train should be reduced before testing could be started for the second phase. One reason for this was that the T&E Facility was not permitted to store reactive wastes, such as cyanide bearing wastewater, in storage tanks for more than eight hours. Reactive wastes had to be stored in sealed drums within a secure drum storage area especially designed for hazardous waste spill containment. Therefore, it was necessary to build a special drum handling area adjacent to the project site. Drums were located in a manner to facilitate the pumping of waste directly into the system and to collect the process effluents into receiving drums. This drum handling area also was designed to contain spills, including a vented enclosure to contain and treat any accidental releases of toxic gases, such as, hydrogen cyanide or cyanogen chloride. This same drum handling area can also be used for handling other wastes (e.g. organic wastes) which will be used for other projects.

A two stage alkaline chlorination unit has been set up for the cyanide destruction. In the first stage, at a pH of 11 to 12 cyanide is oxidized to the less toxic cyanate. In the second stage, cyanate is further oxidized to carbon dioxide and nitrogen. Second stage oxidation proceeds faster at lower pH. However, at pH below 8.0 there is considerable risk of toxic gas (hydrogen cyanide, cyanogen chloride and chlorine) generation. A pH of 8.5 is considered optimum for the second stage. In both stages pH and ORP controllers will be used to dispense the reagents. A 15% sodium hypochlorite solution will be used as the oxidizing agent. The appropriate dose and the optimum retention time will be determined by bench scale testing for each cyanide concentration. Set points for the ORP controllers will be determined by testing the reactor effluents for excess chlorine using potassium iodide starch paper. Typical values of operating parameters encountered in the industry are:

pH in first stage:	11.5
pH in second stage:	8.5
ORP in first stage:	350 mV
ORP in second stage:	700 mV
Retention time in first stage:	1 hr
Retention time in second stage;	1 hr

A 50% sodium hydroxide solution and 5% sulfuric acid will be used as the pH controlling reagents. A flow rate of 0.5 gpm will be used for the alkaline chlorination unit. Process optimization is underway for the first cyanide waste.

The effluent from the alkaline chlorination unit will be treated for metals removal using the following processes in series: lime

precipitation, sulfide precipitation, mixed-media filtration and ion exchange adsorption. Activated carbon will be used for the removal of organics. Process optimization for each of these units will be performed using the effluent from the preceding unit.

Cyanide concentrations will be measured by an Ion Chromatographic method recently developed by the EPA (Wilson et al, 1986). This method has been validated by comparison with EPA method 335.2. In addition to the critical measurements of metals and cyanide concentrations, all wastes will be analyzed for other priority pollutants such as volatile and semivolatile organics, PCBs, fluorides and sulfides. Other significant parameters such as pH, ammonia content, chemical oxygen demand, total and dissolved solids, total organic halides and EDTA concentrations will be measured. Standard EPA methods, as prescribed in EPA SW-846, will be followed for all analyses.

CONCLUSIONS

As a result of the phase I testing, it was determined that addition of ferrous sulfide and polyelctrolytic flocculant in the precipitation/ clarification step enhanced the effluent quality. Nickel and copper were difficult to remove as a result of possible complex formations with chelating agents. Ion exchange polishing markedly improved the effluent quality while mixed-media filtration provided little treatment enhancement.

REFERENCES

1. Durney, L.J., Electroplating Engineering Handbook, 4th ed., 1984.

2. Grosse, D.W., "Treatment Technologies for Hazardous Wastes: Part IV: A Review of Alternative Treatment Processes for Metal Bearing Hazardous Waste Streams" JAPCA, 36 (5), May 1986.

3. Grosse, D.W. et al., "Treatment of Aqueous Metal Bearing Hazardous Wastes," Proceedings of the 8th AESF/EPA Conference on Pollution Control for the Metal Finishing Industry, San Diego, February 11, 1987.

4. Patterson, J.W., Industrial Wastewater Treatment Technology, 2nd ed., 1984.

5. Peters, R.W. et al., "Evaluation of Recent Treatment Techniques for Removal of Heavy Metals from Industrial Wastewaters," AIChE Symposium Series, 81 (243), 165-203, 1985.

6. Sanks, R.L., Water Treatment Plant Design for Practicing Engineers, 1978.

7. Wilson, D.L. et al., Determination of Cyanide in Aluminum Industrial Wastewater by Ion Chromatographic and Spectrophotometric Techniques, LC-GC, 4, (6), 578, 1986.

8. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Rev. March 1983.

9. Test Methods for Evaluating Solid Waste, EPA-SW-846, 3rd ed. November 1986, Office of Solid Waste and Emergency Response.